A Leather Finishing Agent

The invention relates to a liquid agent having a long shelf life, which is used in wet dressing of leather and enables simultaneous retanning, lubricating and other finishing of leather in a single bath.

Wet dressing of leather comprises several operations. During neutralization, the pH value is regulated as required in further processes, using inorganic or organic salts with alkaline reaction. Lubrication is responsible for the softness of the leather by incorporating lubricating substances reducing the friction between structural elements of the leather. In retanning, at last, leather character, body, and grain crack resistance, among other things, are adjusted using vegetable, mineral or synthetic tanning agents. These operations are carried out successively, partially in separate baths. The current state of development has been described in e.g. Magerkurt, B.: "Aktuelle Gesichtspunkte und Stand der Technik im Bereich der Naßzurichtung und Zurichtung", in: Das Leder H.1, 1996, pp. 7-14, and in "Bibliothek des Leders", Vol. 3, Faber, K., "Gerbmittel, Gerbung und Nachgerbung" (Umschau Verlag, Frankfurt/Main, 1984), and Vol. 4 Hollstein, M., "Entfetten, Fetten und Hydrophobieren bei der Lederherstellung" (Umschau Verlag, Frankfurt/Main, 1987).

To achieve an efficient procedure, numerous attempts have been made to combine the individual, or all of the subprocesses into a single operation. Thus, for example, Wachsmann, H. in: Das Leder, H.6, 1981, pp. 109-112, describes a compact procedure wherein all of the operations are carried out in a single bath, yet still in succession, using a variety of different products. At the same time, Wachsmann points out the difficulties arising therein,

namely, the compatibility of the products employed. Indeed, the main problem is that the products required for these sub-processes are not miscible with each other, being unstable in the production of use-relevant emulsions, separating into their components, or even causing mutual precipitation. Even when using conventional emulsifiers, the production of stable, liquid formulations that would also yield stable emulsions has not been possible as yet.

DE-OS 196 53 549 therefore provides a preferably solid agent for such a compact product, i.e., the components required must be subjected to e.g. spray drying in order to obtain a form having long shelf life. Explicit reference is made to the instability of liquid formulations. Even when producing an at least eightfold dilution, the way in which these formulations are commonly used, no stable emulsions are being formed wherein the micelles would include both tanning agent and lubricant molecules. This can only be achieved temporarily by using ultrasound. However, an ultrasonic treatment of the emulsions prepared a short time prior to use is complex and generally not available to the users of these products.

However, solid products involve several serious drawbacks. Their production requires a high input of energy which does not seem justified as a result of the fact that only dissolved, liquid products can be used, i.e., all of the solids must be dissolved prior to or during treatment. Handling and metering are somewhat complex. As a rule, metering means for powdered products are not available in leather factories, so that the large amounts required have to be metered manually. On the other hand, leather factories are equipped with metering units for liquids. Salts such as sodium sulfate are used as carrier substances which pollute the environment but do not have any positive effect in use-related terms. On the contrary, adverse effects on

the leather may even occur. Thus, the important quality parameter regarding leachable inorganic compounds (DIN 53307) may be exceeded as a result of the high salt concentrations, which in turn may give rise to salt efflorescence on the leather or necessitate additional water-consuming washing processes.

It was therefore the object to find an agent which has both tanning and lubricating properties, as well as pH value-regulating properties, and which is present at room temperature in a liquid form having long shelf life. When diluted with water, a stable emulsion should be formed wherein the micelles would include both tanning agent and lubricant molecules. Thus, the agent must permit a compact procedure in wet dressing, i.e., at least the operations of neutralizing, retanning and lubricating in a single step. For this reason, the agent must include lubricants, retanning agents, substances regulating the pH value, and optionally further additives as components.

Surprisingly, it has now been found that when using lubricants based on natural or synthetic unsaturated fats, oils or waxes subjected to an oxidative treatment prior to further chemical reaction, stable, liquid mixtures with tanning agents and substances regulating the pH value are obtained, which form entirely stable emulsions upon further dilution with water.

The inventive liquid agent which is stable on storage and in emulsion and is used in wet dressing of leather and fur, enabling the operations of neutralizing, retanning and lubricating in a single bath in one single step, includes lubricants, retanning agents, substances regulating the pH value, and optionally further additives as components, and is characterized in that unsaturated fats, oils or waxes of natural or synthetic origin are used as starting materials

in the production of said lubricant, which are subjected to an oxidative treatment prior to further chemical reaction.

The inventive oxidative treatment of the unsaturated fat, oil and wax starting materials must be effected in a way so as to reduce the iodine number by at least 20 units, but preferably by about 30 to 40 units. The oxidation can be performed by introducing atmospheric oxygen at temperatures between 70 and 120°C, or by using suitable oxidizing agents such as hydrogen peroxide.

Following said oxidation process, further chemical reaction to yield the lubricant is effected in a well-known manner, e.g. by sulfation, sulfochlorination, phosphating, ethoxylation, amidation, or by preparing the corresponding sulfosuccinates, with the aim of rendering the water-insoluble fats, oils and waxes emulsifiable in water.

The basis for the lubricant component are all those natural or synthetic fats, oils and waxes which have sufficient unsaturated bonds so as to be susceptible to an oxidation process. Among the large number of potential starting materials, lubricant components of natural origin may be exemplified as follows: fish oils, colza oil, soya oil, lecithin, and many others. Lubricant components of synthetic origin are e.g. polyunsaturated hydrocarbons with a chain length $>C_{12}$, unsaturated fatty alcohols with a chain length $>C_{12}$, unsaturated fatty acids with a chain length $>C_{12}$, or esters of unsaturated fatty acids.

Well-known vegetable and synthetic tanning agents are possible as retanning agents. Vegetable tanning agents are extracts from plants or plant parts (e.g. bark, fruits, wood, roots) containing pyrogallol or catechol and/or derivatives thereof. Synthetic tanning agents are e.g. condensation products of formaldehyde with aromatic compounds which may

also be present in their sulfonated form. Said condensation products can be processed further in the form of the free sulfonic acid or the lithium, sodium, potassium or ammonium salts thereof. Furthermore, condensation products of formaldehyde with nitrogen bases such as urea, melamine, thiourea, and dicyandiamide are possible as tanning agent component. Synthetic tanning agents also include polymer tanning agents which are water-soluble polymers based on acrylate, polyurethane or polybutadiene. Aldehyde tanning agents such as glutaric aldehyde, acetaldehyde and propionaldehyde and other aliphatic aldehydes, as well as aldehyde acids such as glyoxylic acid are also possible. A detailed illustration and description of possible vegetable and synthetic tanning agents is given in Kurt Faber, "Gerbmittel, Gerbung und Nachgerbung" from the series "Bibliothek des Leders", Vol. 3 (Umschau Verlag, Frankfurt 1985).

Exemplary substances regulating the pH value include: alkaline earth oxides, alkali and alkaline earth hydroxides, ammonium compounds, as well as other inorganic and organic salts showing a basic reaction.

Said optional other components are understood to be materials which do not necessarily have to be components of the agent according to the invention, yet can be a component that is required in a formulation in a particular case. They include solvents such as alcohols or hydrocarbons, preservatives, antioxidants, fillers such as urea or rock salt, viscosity regulators such as mineral oils of varying viscosity, etc..

Accordingly, the agent of the invention includes the following components (in wt.-%):

a)	lubricant	10-90%, preferably 20-80%
b)	tanning agent	10-90%, preferably 20-80%
c)	pH-regulating substances	1-30%

and optionally

d) other additives 0-30%

The components are mixed and homogenized by stirring, e.g. in a stirred reactor at temperatures between 20 and 90°C, preferably at temperatures between 30 and 60°C. There are no particular requirements as to the design of the stirring apparatus. The products obtained are clear, liquid and entirely stable when stored. Storage stability is ensured both at low temperatures, e.g. down to -30°C, and high temperatures, e.g. up to 60°C.

By using the agents according to the invention, the formulations for leather wet dressing are simplified considerably. Following washing of the leather so as to remove shavings and possible dirt, water in an amount of 20-200%, preferably 50-150% (relative to the shaving weight), and 5-30%, preferably 10-25% of the agent according to the invention are added to the leather. As a rule, the agent of the invention is pre-emulsified using a four- to eightfold amount of water, thereby forming an entirely stable, opaque emulsion, the micelles of which include both tanning agent and lubricant molecules. These emulsions are stable over a long period of time, with no separation into the components occurring. However, direct metering without previous preparation of an emulsion is also possible. The process temperatures are from 20 to 60°C, preferably from 30 to 50°C.

Following a treatment period of 1-4 hours, preferably 2-3 hours, a pH value of from 3.5 to 3.8 is adjusted using organic acids, and the leathers are finished in a conventional operation. Dyeing of the leathers can be performed either by adding a dye during the aforementioned process or in a subsequent, additional operation.

Using the agent according to the invention, virtually all types of leather such as furniture leathers, car upholstery leathers, leathers for shoe manufacturing, clothing leathers, as well as technical leathers can be produced. The composition of the agent of the invention can be varied depending on the requirements to be met by the leather to be produced. Thus, for example, strong, firm types of leather require a higher percentage of tanning agent and a lower percentage of lubricant. Correspondingly, the amount of lubricant prevails in soft types of leather. Obviously, the type of components incorporated in the product also has an influence on the leather character of the resulting leather. Such variations of composition do not adversely affect the stability properties of the inventive agents and emulsions thereof.

The use of the liquid agent according to the invention offers a variety of advantages to the user. Not more than one single product is necessary in wet dressing, which product can be stored in a tank and metered automatically. This is advantageous both in logistic and cost-related terms. The exceedingly short process time represents a gain in capacity, saving possible investment cost. As a result of such simultaneous processing, significant amounts of water and waste water are saved, which is advantageous both in cost-related and ecological terms.

With reference to the examples, the production and use of the agent according to the invention will be illustrated in more detail below.

Production example 1:

Component A (lubricant): colza oil having an iodine number of 110 is oxidized at 90°C with atmospheric oxygen down to

an iodine number of 80. After completed oxidation, this is ethoxylated using 10 mol of ethylene oxide and subsequently sulfonated to obtain a content of organically bound SO_3 of about 2.0%.

Component B (tanning agent): synthetic tanning agent based on a condensation product of phenolsulfonic acid, phenol, urea, and formaldehyde, and having a dry substance of 50%.

Component C (pH-regulating agent): sodium formate, monoethanolamine.

In a stirred reactor, 58 parts of component A and 30 parts of component B are added with 10 parts of sodium formate and 2 parts of triethanolamine and stirred to homogeneity at 60°C. A water content of 40% is adjusted by adding decarbonized water. A golden yellow, oily product is formed, which is entirely stable when stored within a temperature range of from -20 to +50°C and forms entirely stable, finely disperse emulsions upon dilution with water.

Production example 2:

Component A (lubricant): fish oil having an iodine number of 130 is mixed homogeneously with tall oil fatty acid methyl ester having an iodine number of 155 at a ratio of 1:1, and this is subjected to an oxidation with atmospheric oxygen at 110°C. The reaction is carried out until an iodine number of the mixture of 100 is reached. The reaction product subsequently is subjected to sulfonation and neutralized with triethanolamine. The product has a content of organically bound SO_3 of 4.5%.

Component B (tanning agent): a condensation product of formaldehyde and dihydroxydiphenylsulfone having a dry substance of 45% and a Na polyacrylate having an average molar

mass of 25,000 g/mol and a dry substance of 35% are mixed to homogeneity at room temperature.

Component C (pH-regulating agent): ammonium acetate, triethanolamine.

Component D: urea, chloroacetamide.

In a stirred reactor, 35 parts of component A, 50 parts of component B, 5 parts of ammonium acetate, 0.5 parts of triethanolamine, 9 parts of urea, and 0.5 parts of chloroacetamide are mixed to homogeneity at 50°C and adjusted to a water content of 60% using decarbonized water. The pH value is checked and optionally adjusted to 7.8 - 8,2 using triethanolamine. A dark-brown, clear product is formed which is stable when stored. A milky-opaque, stable emulsion is formed upon dilution with water at a ratio of 1:10.

Use example 3:

Australian sheep pickled pelts were subjected to a conventional chrome tanning. The "wet blues" thus obtained were shaved to 0.6 mm and finished according to the following compact formulation using the inventive agent from Example 1, wherein neutralizing, tanning and lubricating were performed simultaneously in one single bath. The agent from Example 1 was emulsified at a temperature of 40°C, using the fivefold amount of water. The percentages relate to the shaving weight.

Operation	Agent	Amount	Temp.	Time	pH
Washing	Water	200%	30°C	20 min	3.8
Discharge bath					
Neutralization/	Water	150%			
Retanning/	Agent from Example 1	20%	40°C	90 min	5.9
Lubrication	Pre-emulsified with water 1:5				
Dyeing	Anionic dye	3%		90 min	
Acidification	Formic acid 85%	1.5%		60 min	3.8
Washing	Water	200%	30°C	20 min	

The leathers were finished according to conventional operation, and they were soft, grain crack-resistant and exhibited even dyeing.

Use example 4:

Cowhide "wet blues" from Southern German crude hides with a shaving thickness of 1.2 mm were processed into furniture leather according to the following formulation, using the agent from Example 2. The agent from Example 2 was employed directly without previous emulsifying. The percentages relate to the shaving weight.

Operation	Agent	Amount	Temp.	Time	pH
Washing	Water	200%	30°C	20 min	3.9
Discharge bath					
Neutralization/ Retanning/ Lubrication	Water Agent from Example 2	100% 19%	40°C	90 min	6.2
Dyeing	Anionic dye	4%		90 min	
Acidification	Formic acid 85%	2%		60 min	3.7
Washing	Water	200%	30°C	20 min	

The leathers were finished according to conventional operation. The finished leathers were remarkable for their softness with simultaneous grain crack resistance and fine, even grain. Dyeing was even with respect to surface and cross-section.